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54 A catalyst diluent.

57 Disclosed is a catalyst diluent which is made up of a  
graphite in a columnar shape having a diameter of between  
3 and 6 mm and a height of between 3 and 6 mm. The  
catalyst diluent produces the desired product in a high yield  
while preventing local overheating portion in a catalyst bed.

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## A CATALYST DILUENT

BACKGROUND OF THE INVENTION1. Field of the Invention

5           The present invention relates to a novel diluent  
suitable for a solid catalyst in use for a fixed bed  
reactor. More specifically, it relates to an improved  
catalyst diluent which produces the desired product  
in a high yield while preventing overheating portion  
10       from taking place locally in a catalyst bed in a  
reaction accompanying huge heat generation.

2. Description of the Prior Art

          In practicing a reaction such as an oxychlorination  
reaction of ethylene, accompanying huge heat generation,  
15       one of the problems to be given care to is control of  
the reaction temperature. Stated generally, the thermal  
conductivity of a catalyst per se is low and thus  
inviting local formation of overheating portion in a  
catalyst bed. The local formation of overheating  
20       portion inevitably brings about a danger such as runaway  
of reaction, explosion and the like, and even when such  
a danger is prevented, it increases undesired side  
reactions such as decomposition to thereby lower  
selectivity of the desired product. Still worse, the  
25       formation of local overheating portion promotes  
disadvantageously corrosion of the reactor as well as

reduction in catalytic performance.

In order to eliminate the foregoing defects in effecting exothermic reactions, there is proposed a process for diluting a catalyst with inert substance particles. As the inert substance particles used for this purpose, silica, alumina, glass beads, graphite, silicon carbide and the like are suggested.

Notwithstanding, when silica, alumina and glass beads are used, the mixing ratio to the catalyst has to be increased to prevent the generation of local overheating portion since the thermal conductivity of these substances is not so high as compared with that of activated alumina, silica alumina and the like widely used as a catalyst and a carrier. As a result, productivity per unit volume of a reactor is forced to be reduced. Moreover, those normally possess approximately twice the apparent specific gravity of the catalyst particles and hence a heterogeneous mixture tends to result when a catalyst is mingled with those diluents. As far as silicon carbide and graphite are concerned, it is pointed out that they cause chemical reaction and degradation in catalytic activity, while exhibiting superior thermal conductivity (Japanese Patent Examined Publication No. 7948/1966). The present inventors have carried out an oxychlorination reaction of ethylene using those diluents commercially available

and ascertained that ethyl chloride was prepared in a greater amount than the case where  $\alpha$ -alumina was employed as a diluent, and that no difference was observed, as compared with  $\alpha$ -alumina, in an effect of controlling reaction temperature. Moreover, the diluents used heretofore have, as a whole, neither substantially the same size nor the same shape, which also causes a heterogeneous mixture.

Another process is proposed to solve the foregoing drawbacks in which the reaction temperature and local overheating is controlled by a combination of several kinds of catalysts having different catalytic activities, without using a diluent. The process, however, is also disadvantageous in that the thermal conductivity of the catalyst particles is so low that it is rather difficult to control overheating portion as compared with the case where a diluent is used.

A series of studies have been made by the present inventors as to a catalyst diluent which not only eliminates the foregoing drawbacks of those known diluents including formation of local overheating portion and a decrease in selectivity as well as catalytic performance, but is capable of enhancing the mixing ratio of a catalyst to a diluent, and the inventors have discovered that only graphite particles in a columnar shape having the specified dimensions

achieve these objects.

#### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a catalyst diluent generating no formation  
5 of local overheating portion in the catalytic fixed bed.

It is another object of the present invention to provide a catalytic diluent which is capable of increasing the mixing ratio of a catalyst to the diluent and providing a uniform mixture with the catalyst.

10 It is a further object of the present invention to provide a catalyst diluent exhibiting a superior selectivity and preventing degradation in catalytic performance.

These and other objects of the present invention  
15 together with the advantages thereof will become apparent to those skilled in the art from the detailed disclosure of the present invention as set forth hereinbelow.

The present invention encompasses a catalyst diluent suitable for a fixed bed exothermic reaction  
20 which is made up of a graphite in a columnar shape having a diameter of a circular portion of between 3 and 6 mm and a height of between 3 and 6 mm, or having dimensions within the foregoing ranges in a substantially predominant quantity.

#### 25 DETAILED DESCRIPTION OF THE INVENTION

The diluent of the present invention may most

preferably be in a columnar shape having a diameter of a circular portion of between 4 to 5.5 mm and a height of between 4 to 5.5 mm, or having dimensions within the foregoing ranges in a substantially predominant quantity. In cases where the diameter is more than 6 mm, the thermal conductivity, when mixed with catalyst particles, becomes inferior and uniform and intimate mixing with the catalyst particles is not feasibly provided. Inversely, in cases where the outer diameter is less than 3 mm, there are brought about problems such as increased pressure loss exerted on the effluent and increased cost in manufacture. The diluent of the present invention is not necessarily required to possess a complete circle or a circle close thereto as a circular portion of a columnar shape, an oval shape is also within the present invention which provides a satisfactory result. Although it has been known to be able to employ graphite particles as a catalyst diluent, the graphite particles of an irregular shape such as a broken shape or of a great porosity having an apparent specific gravity of less than 1.5 have been used, and thus superior thermal conductivity a graphite per se possesses has not been made the most of. In addition, they exhibit undesired reactivity including an increase in side reactions and hence they are rarely used today.

According to experimental results made by the present inventors, they only showed almost the same temperature controlling effect as the other diluents such as  $\alpha$ -alumina and even spherical graphite particles also demonstrated similar results. Inversely, the graphite particles having a specified shape of the present invention have been found to produce an outstanding effect of controlling temperature in a catalytic bed as a diluent, thus the present invention being completed.

Another prominent advantage of the diluent of the present invention is to increase the mixing ratio of a catalyst to the quantity of the diluent, so that degradation in catalytic activity is not only reduced relatively, but productivity per unit volume of a reactor is raised.

A further advantage of the diluent of the present invention is to prevent the occurrence of local overheating portion owing to the irregularity of mixing, because it possesses an apparent specific gravity close to that of catalyst particles commonly employed to thereby facilitate uniform and intimate mixing.

On the other hand,  $\alpha$ -alumina, fused silica and silicon carbide possess a fairly large apparent specific gravity as compared with a catalyst supported on activated alumina as a carrier and, in consequence, uniform and intimate mixing with a catalyst is not so easy. The

heterogeneous mixing also leads to a disadvantage that local overheating portion is likely to take place.

5       The material of the diluent of the present invention is a graphite, which is generally produced by mixing tar and pitch with petroleum coke, pitch coke, carbon black and the like, molding the mixture, heating it at first at a temperature between 1,000 and 1,300°C and thereafter sintering at a temperature between 2,000 and 3,000°C. A columnar shaped graphite of the present invention may be obtained by molding the mixture by  
10       a compression type pelletizer after mixing and prior to sintering or by extruding the mixture into a rod shaped article, then cutting it after heating or sintering to be a desired height.

15       The diluent of the present invention need not be a pure single crystal graphite but may preferably be one having a specific gravity of 2.0 or more and an apparent specific gravity of 1.5 or more to enhance a temperature controlling effect as a diluent.

20       As regards undesired reactivity and degradation in catalytic activity which were deficiencies in the case where the conventional graphite particles were used as a catalyst diluent, the present inventors have discovered after an extensive study that these deficiencies  
25       are caused by iron remained or entered during the manufacturing, and that the foregoing deficiencies can be

eliminated by reducing the amount of iron contained in  
or deposited to the graphite particles to 0.1 percent by  
weight, more preferably 0.05 percent by weight. The  
graphite particles containing of iron in an amount of  
5 0.1 percent by weight or less are obtained by the use of  
materials with a low content of iron such as petroleum  
coke, pitch coke, carbon black, tar pitch and the like  
and further by preventing iron from mixing into or  
depositing on the graphite particles from the outside.  
10 The graphite particles with a low content of iron may  
also be prepared by washing out iron contained or  
deposited with hydrochloric acid and the like.

When the diluent of the present invention is  
employed on an industrial scale, the diameter of catalyst  
15 particles should preferably be close to that of the  
diluent but is not specifically limited thereto. The  
catalyst may be in any shape such as sphere, column,  
ring, singly or in conjunction with two or more.  
Above all, the most preferable as a catalyst is a cylin-  
20 drical shape the present inventors made a patent  
application earlier (Japanese Patent Application No.  
45925/1980) and when the cylindrical shaped catalyst is  
used in conjunction with the diluent of the present  
invention, the characteristics the both possess  
25 inherently are markedly enhanced to produce unexpected  
synergistic effects. Furthermore, the catalyst mixed

with the diluent of the present invention is not limited to one sort, but used in combination with one or more sorts of catalysts which are different in composition, activity and shape. The foregoing applications are also  
5 included in the scope of the present invention.

As the reaction that marked effects can be expected by effecting a contact reaction in a fixed bed containing the present diluent on an industrial scale, there are included, by example, an oxychlorination reaction, a  
10 vapor phase chlorination, a vapor phase hydrogenation and a vapor phase oxidation.

Hereinafter the present invention will be explained in more detail relating to an oxychlorination reaction producing ethane dichloride, comparing the examples  
15 with the comparative examples, to which the present invention is not construed to be limited.  
EXAMPLES 1 to 6, COMPARATIVE EXAMPLES 1 to 5.

A reactor used for reaction was a vertical type reactor of a nickel tube having an interior diameter  
20 of 26.3 mm and a length of 1,200 mm to the entirety of which a jacket was welded, through which a heating medium (DOWTHERM E, trademark of Dow Chemical Japan Co.) was permitted to be recycled in a state of liquid.  
At an inlet and an outlet of the reactor, were manometers provided to measure the flow resistance through  
25 the packed layer of a catalyst and a diluent. A reactant

gases were introduced from the upper portion of the reactor. The gases reacted were led from the lower portion of the reactor to the outside of the reactor, cooled at two stages, i.e., first to 5°C and second to  
5    -35°C to condense condensable reaction products, then the resultant condensates and non-condensed gases being subjected to the analysis by a gaschromatography in a normal manner.

As a catalyst, a commercially available spherical  
10    catalyst made up of a system of  $\text{CuCl}_2$ - $\text{KCl}$ - $\gamma\text{Al}_2\text{O}_3$  (20 percent of  $\text{CuCl}_2$  and 2.3 percent of  $\text{KCl}$  are contained and the diameter is 5 to 6 mm, hereinafter referred to as "Catalyst A") or a ring-shaped catalyst made up of a system of  $\text{CuCl}_2$ - $\text{KCl}$ - $\gamma\text{Al}_2\text{O}_3$  (18 percent of  $\text{CuCl}_2$  and 1.5  
15    percent of  $\text{KCl}$  are contained and the height is 5 mm, the outer diameter is 5 mm and the inner diameter is 2.2 mm, hereinafter referred to as "Catalyst B") prepared by the inventors was employed.

The foregoing catalysts were respectively mixed  
20    adequately with a variety of diluents to prepare an intimate mixture and 205 ml of the mixture were packed into the upper portion of the reactor and 205 ml of the non-diluted catalyst were packed into the lower portion of the reactor, then the reaction was allowed to take  
25    place. The reactant gases were introduced into the reactor, respectively, at a rate of 40 Nl/hr for hydrogen

chloride, 21.6 Nl/hr for ethylene and 57 Nl/hr for  
air. The pressure at the outlet of the reactor was  
maintained at atmospheric pressure. The reaction  
temperature was controlled by the adjustment of the  
5 temperature of a heating medium in the jacket so that  
conversion of hydrogen chloride introduced might come  
to 99 percent. The obtained results were given in  
Table 1.

TABLE 1

|                                       | Ex. 1    | Ex. 2    | Ex. 3    | Ex. 4    | Ex. 5    | Ex. 6    |
|---------------------------------------|----------|----------|----------|----------|----------|----------|
| Catalyst diluent                      |          |          |          |          |          |          |
| Sort                                  | Graphite | Graphite | Graphite | Graphite | Graphite | Graphite |
| Shape                                 | Column   | Column   | Column   | Column   | Column   | Column   |
| Diameter (mm)                         | 5        | 6        | 4        | 5        | 5        | 5        |
| Height (mm)                           | 5        | 6        | 4        | 5        | 5        | 5        |
| Content of iron (wt%)                 | 0.03     | 0.02     | 0.03     | 0.02     | 0.2      | 0.04     |
| Apparent specific gravity             | 1.6      | 1.6      | 1.6      | 1.6      | 1.6      | 1.45     |
| Catalyst                              | A        | A        | A        | B        | A        | A        |
| Heat medium temp. ( $T_1$ ) (°C)      | 205      | 202      | 207      | 201      | 204      | 200      |
| Highest reaction temp. ( $T_2$ ) (°C) | 285      | 288      | 284      | 270      | 285      | 290      |
| $T_2 - T_1$ (°C)                      | 80       | 86       | 77       | 69       | 81       | 90       |
| Selectivity (%)                       |          |          |          |          |          |          |
| 1,2-Dichloroethane                    | 97.4     | 96.9     | 97.6     | 98.7     | 96.6     | 96.6     |
| Ethyl chloride                        | 0.4      | 0.5      | 0.4      | 0.2      | 0.8      | 0.5      |
| Other halides                         | 0.9      | 1.0      | 0.8      | 0.5      | 1.1      | 1.2      |
| Combustion rate of ethylene (%)       | 1.3      | 1.6      | 1.2      | 0.6      | 1.5      | 1.7      |
| Conversion of HCl (%)                 |          |          |          |          |          |          |
| Initial stage of reaction             | 99.0     | 99.1     | 99.1     | 99.2     | 98.8     | 99.0     |
| After 500-hour reaction               | 98.7     | 98.7     | 98.7     | 98.8     | 98.3     | 98.4     |

|                                       | Comp.<br>Ex. 1 | Comp.<br>Ex. 2 | Comp.<br>Ex. 3 | Comp.<br>Ex. 4    | Comp.<br>Ex. 5  |
|---------------------------------------|----------------|----------------|----------------|-------------------|-----------------|
| Catalyst diluent                      |                |                |                |                   |                 |
| Sort                                  | Graphite       | Graphite       | Graphite       | $\alpha$ -alumina | Silicon carbide |
| Shape                                 | Sphere         | Broken shape   | Column         | Sphere            | Sphere          |
| Diameter (mm)                         | 4-6            | 3-7            | 7              | 5-6               | 4-6             |
| Height (mm)                           | -              | -              | 7              | -                 | -               |
| Content of iron (wt%)                 | 0.03           | 0.08           | 0.03           | 0.02              | 0.10            |
| Apparent specific gravity             | 1.6            | 1.45           | 1.6            | 3.4               | 2.2             |
| Catalyst                              | A              | A              | A              | A                 | A               |
| Heat medium temp. ( $T_1$ ) (°C)      | 195            | 196            | 198            | 192               | 190             |
| Highest reaction temp. ( $T_2$ ) (°C) | 300            | 298            | 277            | 303               | 305             |
| $T_2 - T_1$ (°C)                      | 105            | 102            | 99             | 111               | 115             |
| Selectivity (%)                       |                |                |                |                   |                 |
| 1,2-Dichloroethane                    | 95.7           | 95.9           | 96.1           | 95.1              | 94.7            |
| Ethyl chloride                        | 0.7            | 0.8            | 0.7            | 0.8               | 0.9             |
| Other halides                         | 1.4            | 1.3            | 1.3            | 1.6               | 1.8             |
| Combustion rate of ethylene (%)       | 2.2            | 2.0            | 1.9            | 2.5               | 2.6             |
| Conversion of HCl (%)                 |                |                |                |                   |                 |
| Initial stage of reaction             | 99.2           | 98.9           | 99.0           | 99.1              | 99.0            |
| After 500-hour reaction               | 98.1           | 98.0           | 98.2           | 97.8              | 97.5            |

The highest temperature portion (hot spot) was found to be present in the upper portion of the reactor, i.e., in the portion where the diluent was mixed in every example and comparative example.

- 5        It is understood from the results of Table 1 that the diluent of the present invention is superior in thermal conductivity and reaction results, as compared with graphite particles in other shapes, and  $\alpha$ -alumina and silicon carbide commonly employed.

## WHAT WE CLAIM IS:

1. A catalyst diluent for use in a fixed bed exothermic reaction which comprises a graphite in a columnar shape having a diameter of a circular portion of between 3 and 6 mm and a height of between 3 and 6 mm.
2. The catalyst diluent of Claim 1, wherein the apparent specific gravity of the graphite is 1.5 or more.
3. The catalyst diluent of Claim 1, wherein the amount of iron deposited onto or contained in the graphite is 0.1 percent or less.
4. The catalyst diluent of any preceding Claims 1 to 3, wherein the fixed bed exothermic reaction is an oxychlorination reaction of ethylene.
5. The catalyst diluent of Claim 1, wherein a catalyst used is in a cylindrical shape in a substantially predominant quantity.
6. The catalyst diluent for use in a fixed bed exothermic reaction which comprises, in a substantially predominant quantity, a graphite in a columnar shape having a diameter of a circular portion of between 3 and 6 mm and a height of between 3 and 6 mm.
7. The catalyst diluent of Claim 6, wherein the apparent specific gravity of the graphite is 1.5 or more.
8. The catalyst diluent of Claim 6, wherein the

amount of iron deposited onto or contained in the graphite is 0.1 percent or less.

5        9. The catalyst diluent of any preceding Claims 6 to 8, wherein the fixed bed exothermic reaction is an oxychlorination reaction of ethylene.

10. The catalyst diluent of Claim 6, wherein a catalyst used is in a cylindrical shape in a substantially predominant quantity.



European Patent  
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# EUROPEAN SEARCH REPORT

0060317  
Application number

EP 81 10 6730

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |  |   |
|---|---|--|---|
| Category  | Citation of document with indication, where appropriate, of relevant passages           | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)                                |
| A   | FR-A-2 231 621 (KUREHA KAGAKU KOGYO)<br>& US - A - 3 953 345                            |  | B 01 J 37/04<br>B 01 J 35/02<br>B 01 J 21/18<br>B 01 J 27/10<br>C 07 C 17/156 |
| A   | FR-A-2 390 381 (LE CARBONE LORRAINE)<br>& US - A - 4 205 055                            |  |   |
| A   | GB-A-1 373 351 (MONSANTO)   |  |   |
| A   | FR-A-2 132 795 (TRUST CESKOSLOVENSKEHO PRUMYSLU DUSIKARENSKEHO)<br>& US - A - 3 853 790 |  |   |
| A   | FR-A- 510 948 (BREMEN BESIGHEIMER OELFABRIKEN)  |  | TECHNICAL FIELDS SEARCHED (Int. Cl. 3)  |
| A   | GB-A- 792 706 (STANDARD OIL)  |  | B 01 J<br>C 07 C  |
| The present search report has been drawn up for all claims  |   |  |   |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>23-06-1982   | Examiner<br>THION M.A.  |
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